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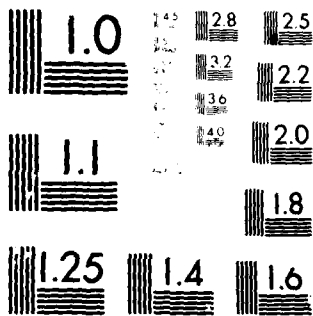UNCLASSIFIED   NL

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CHEMISORBED OVERLAYER

by

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September 14, 1979

ISLAND FORMATION AND CONDENSATION OF A

CHEMISORBED OVERLAYER*

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Abstract

The condensation of a chemisorbed overlayer from a lattice gas into a particular ordered structure is discussed in terms of the lattice-gas theory of Lee and Yang. The formation of islands of ordered structure is identified with the condensation phenomenon predicted by the theory. The phase diagram (transition temperature vs. coverage) based on the theory of a two-dimensional Ising ferromagnet in zero magnetic field is constructed for the condensation of a lattice gas system with net attractive interactions between the particles. It is demonstrated that critical points at coverages other than $\theta = 0.5$ are achieved for over-layer systems with unit meshes larger than (1×1). Low-energy electron diffraction results of the thermal disordering (island dissolution) for oxygen chemisorbed on W(110) are compared with the theory, and the effect of substrate surface heterogeneity on the phase diagram is discussed.

I. Introduction

In many chemisorption systems, the adsorbate-substrate binding energy dominates the adsorbate-adsorbate interaction, so that the adsorption is "local", in sites determined by the substrate. This leads to the frequently observed commensurate superlattices, with unit meshes some integral of the substrate mesh, e.g., p(2 x 1) or c(2 x 2). Since in such a system, whether it is ordered or not, an overlayer atom will always be found (except near the desorption temperature) in a prescribed localized site that has a definite coordinate vector with respect to some origin, a lattice gas model can be used to study such properties of the overlayer as phase transitions, diffusion, and overlayer ordering.[1-4] Conversely, a fit to experimental quantities can yield adsorbate interaction energies.[5-7]

For many adsorbates, ordered regions of a particular superlattice form at much less than saturation coverage for that structure, as demonstrated by the observation of low-energy electron diffraction (LEED) superlattice reflections of these low coverages. In many cases, it can be demonstrated simply by observation of the diffraction pattern that this requires condensation of islands on the surface. Thus a deficiency p(2 x 1) structure (i.e., one that contains extra vacancies) cannot exist (except in the pathological case of zero interactions) below $\theta = 0.25$ because it would become a p(2 x 2) structure. Since p(2 x 1) structures are frequently observed at coverages as low as $\theta = 0.1$ [e.g., W(110) p(2 x 1)-O] this requires the condensation of p(2 x 1) islands. Thus if an adsorbed species at temperatures high enough so it is disordered is allowed to cool, it will condense into patches of ordered structures in a "sea" of disorder of low density,

similar to three-dimensional condensation or precipitation out of solution. For the range of temperatures and coverages where this happens, the adsorbed species will thus find itself in a two-phase region of ordered structure and lattice gas, with the density of adatoms in the lattice gas just representing the equilibrium "lateral vapor pressure" of the islands. Condensation of islands, of course, requires a net attractive adatom interaction, the "cohesive energy" of the island.

Whereas initially a number of islands should nucleate and grow, thermodynamic equilibrium requires in the absence of external limiting factors that island coalescence takes place (similar to grain growth in three dimensions), eliminating island boundaries until only one large island in the sea remains. We shall note below that substrate hetero-geneity will limit the size of the island, resulting in a large number of independent, smaller thermodynamic systems.

We believe[6] condensation phenomena in chemisorption systems can be described by the lattice gas theory of the Lee and Yang[8] for a number of different superlattice structures, as long as the lattice gas site is properly defined. We have used this approach to extract attractive adsorbate interaction energies in oxygen chemisorbed on W(110) and it has recently also been discussed in a theoretical framework of lattice gas models.[1b] Because we believe this method may be simply applicable in a number of chemisorption systems, we discuss it in detail here and expand on our work in Ref. 6. In the next section, we review the Lee-Yang model and discuss it in terms of chemisorption of commensurate overlayers. In the following section we apply the model to the system W(110) p(2x1)-O. In the last section we summarize the main points and the limitations of this approach.

II. Application of the Lattice Gas Model of Lee and Yang to Chemisorbed Overlayers

In their classic papers[8] on phase transitions of a system of inter-acting particles, Lee and Yang have shown that for a wide class of inter-action potentials the phase transitions involved are related to the analyticity properties of the grand partition function $\mathcal{J}(z,V)$ in the complex fugacity plane z, as the volume V of the system approaches infinity. The equations of state are

$$\beta p = \frac{1}{V} \log \mathcal{J}(z,V)$$

$$\frac{1}{v} = \frac{1}{V} \frac{\partial}{\partial z} \log \mathcal{J}(z,V) \qquad ,$$

(1)

where $\beta = 1/k_B T$, p is the spreading pressure, and v is the specific volume (the volume occupied by one atom), a quantity independent of V. A phase transition will occur when a root z_0 of the equation $\mathcal{J}(z,V) = 0$ approaches the real positive axis in the complex z plane, as the volume $\to \infty$. In particular, for a lattice gas with attractive interactions, (except equal to $+ \infty$ if two atoms occupy the same lattice site) all the roots should lie on a prescribed circle centered at z=0. This implies the system can undergo only one phase transition, if one exists at all. This occurs at the point of intersection of   the circle and the real positive axis.

A model calculation was carried out by Lee and Yang[8] for a system of particles with attractive interactions on a square lattice, where positions can take only discrete values. This was shown to be equivalent to a two-dimensional ferromagnetic system, in which the solution is known exactly when the external magnetic field H = 0. Consider a finite lattice

system with N lattice sites surrounded by a "gas reservoir" which can absorb from or provide gas atoms to the system freely as shown in Fig. 1. Letting $-\varepsilon$ be an attractive nearest-neighbor interaction energy, neglecting all other interactions, and defining

N_a = total number of occupied sites

N_{aa} = total number of nearest-neighbor pairs of atoms,

the grand partition function is given by

$$\mathcal{J}_g (z,N,T) = \sum_{N_a, N_{aa}} z^{N_a} \exp (\beta\varepsilon N_{aa}), \tag{2}$$

where again z is the fugacity and $\beta = 1/k_B T$.

Instead of a lattice gas system, consider Fig. 1 to be a ferromagnetic spin system of interaction energy -J, with N_+, N_-, N_{++} defined to be respectively the number of up spins, down spins, and nearest-neighbor pairs of up spins. For this system the partition function is

$$\mathcal{J}_S(H,N,T) \sim \sum_{N_+, N_{++}} \exp[-2\beta(4J-H)N_+] \exp[4\beta J N_{++}], \tag{3}$$

where H is the applied magnetic field.

For the spin system,

$$N = N_+ + N_-, \tag{4}$$

where N is the total number of spins, and the intensity of magnification is

$$I(H,T) = \frac{N_+ - N_-}{N}. \tag{5}$$

From equations 4 and 5

$$I(H,T) = \frac{2N_+}{N} - 1. \tag{6}$$

We know from the Ising problem that a discontinuity in $I(H,T)$ occurs at $H=0$, with the intensity of magnetization given for $T < T_c$ by

$$I(0^+,T) = -I(0^-,T) = [1 - 1/\sinh^4 2\beta J]^{1/8}, \tag{7}$$

where

$$I(0^-,T) \equiv \lim_{H \to 0^-} I(H,T) \tag{8}$$

and

$$I(0^+,T) \equiv \lim_{H \to 0^+} I(H,T). \tag{9}$$

The magnetic intensity goes to zero at the critical temperature, T_c, which satisfies the Onsager relation.

$$\sinh^2 2\beta_c J = 1, \tag{10}$$

or

$$T_c = J/0.44 k_B. \tag{11}$$

To establish a correspondence between the two systems, let the occupied sites correspond to spin up and the empty sites to spin down. Then, by comparing equations 2 and 3,

$$N_a \to N_+$$

$$-\epsilon \to -4J \tag{12}$$

$$z \to \exp[-2\beta(4J-H)].$$

In the language of the lattice gas system, and from Eq. 6, $\theta \equiv N_+/N = N_a/N$ is defined to be the fractional coverage,

$$I(H,T) = 2\theta (H,T) - 1, \tag{13}$$

or

$$\theta(H,T) = [I(H,T) + 1]/2. \tag{14}$$

Equation (14) represents the connection between the θ-T phase boundary in the lattice gas model and the I-T phase boundary in the Ising model.

The discontinuity in $I(H,T)$ in the Ising problem for $H = 0$ corresponds to an isothermal change of coverage from

$$\theta(<1/2) = \theta(0^-,T) = [I(0^-,T)+1]/2 \tag{15}$$

to

$$\theta(>1/2) = \theta(0^+,T) = [I(0^+,T)+1]/2 . \tag{16}$$

As mentioned above, Lee and Yang have shown that all the zeros of the partition function should lie on a circle in the complex z-plane whose radius is determined by ε. Thus in the thermodynamic limit, $N \to \infty$, at any temperature $T < T_c$ a zero must occur on the positive real axis at $z_0 = \exp(-2\beta\varepsilon)$. θ is discontinuous at the point z_0 and is given by the analog of Eq. 7,

$$[2\theta(0^+,T) - 1] = - [2\theta(0^-,T) - 1] = [1 - 1/\sinh^4 \tfrac{\beta\varepsilon}{2}]^{1/8}. \tag{17}$$

Equation 17 gives the phase boundary of the lattice gas system in terms of coverage. It should be noted that a phase transition can occur at any coverage. This is shown in Fig. 2. Note that the critical point always occurs at $\theta = \theta_c = 1/2$, and the phase diagram is symmetric about $\theta = \theta_c$. The area under curve OAB is the coexistence region between the vapor phase and the condensed ordered phase (islands). The phase boundary represents the locus of temperatures and coverages where the free energies of the two phases are equal and is, of course, a first-order phase boundary, except at θ_c. The densities of the vapor and island that coexist at any temperature are given respectively by the coverage at the tie points. Thus at any temperature the density of gas atoms in the vapor increases with increasing coverage until condensation of islands with density given by the opposite tie point begins. Increasing the coverage further will increase the proportion of islands to vapor until the high-coverage tie point is reached, above which coverage a single island phase is stable and no vapor phase exists. Increasing the coverage still further will make this condensed phase more dense until at $\theta = 1$ the maximum density is reached. Above the critical isotherm, of course, only a gas phase (of varying density as the coverage is changed) is stable.

A rise in temperature at fixed coverage will lead for $\theta < \theta_c$ to the continuous dissolution of islands into the vapor, with the remaining condensed phase decreasing its density until the phase boundary is reached, at which point the concentration of condensed phase goes to zero.

Above $\theta > \theta_c$, a rise in temperature will lead to a continuous "absorption" of vapor phase into the condensed phase, as more and more point defects become thermodynamically stable in it. That is, the condensed phase becomes less and less dense until at the phase boundary, no more vapor phase exists.

This picture can be generalized to chemisorbed layers with a variety of ordered structures by a proper choice of the adsorbate site. The effect of this will be that the critical coverage θ_c as referred to the substrate can be different from $\theta_c = 1/2$. Consider, for example, a p(2 x 1) structure on a square or rectangular mesh. Its saturation coverage corresponds to one half monolayer, i.e., $\theta = 0.5$. If the adsorbed atoms are assumed to sit in a bridge-bonding configuration, they will require two substrate sites each. Thus the "lattice" for the overlayer can be defined so that each overlayer lattice site corresponds to two neighboring substrate sites.[6] Using this overlayer lattice, the Lee-Yang model will give the critical point at $\theta_{coverlayer} = 0.5$, but this corresponds to an actual surface coverage of $\theta = 0.25$. Similarly for a p(5 x 1) structure on a square or rectangular mesh the critical coverage would occur at $\theta = 0.1$ if bridge-bonded sites are assumed. For other structures, similar geometrically possible and physically sound sites can be chosen. Thus for a p(2 x 2) structure on a square mesh, a four-fold coordinated site would give a critical coverage referred to the substrate of $\theta_c = 0.125$, and a ($\sqrt{3}$ x $\sqrt{3}$) structure on a hexagonal mesh gives a critical coverage of $\theta_c = 0.33$. Similar redefinitions of the overlayer lattice have been made in more complex calculations of the phase diagram for Kr on graphite.[2]

In this generalization, the definition of "nearest-neighbor" must be modified to account for the changed adsorbate site. Thus in a p(2 x 2) overlayer structure, nearest neighbors are twice as far apart as in the substrate. In a p(2 x 1) structure, "nearest neighbors" are in fact a different distance away in the two unit-mesh-vector directions. The fact that ordered overlayer islands with such structures do form at low coverages[6,9-12] implies that there must be a net attractive interaction also in the direction of the long dimension of the adsorbate unit mesh. Because the model permits the evaluation of only one unknown, to get a quantitative value for the attractive interaction energy, it must be chosen to be the same for all "nearest neighbors". Whereas in square or hexagonal lattices this choice is self-evident, in lattices with lesser symmetry it may require special justification. Such a case is discussed in Section III. below.

a) Symmetry Breaking

In any physically realistic adsorbed layer with a unit mesh larger than p(1 x 1), there must be repulsive interactions of finite magnitude. Thus it is frequently observed[9-13] that the overlayer structure changes as the coverage is increased, with the additional adatoms filling the previously empty sites, but with lower binding energy.

The consideration of such repulsive sites leads to a breakdown of the symmetry of the phase diagram. In effect, as disordering into these repulsive sites becomes necessary, the "lattice" reverts back to the substrate lattice. This occurs at high coverages for a particular structure. For any non-p(1 x 1) overlayer structure, an order-disorder transition into these repulsive sites can occur. At saturation coverage

for the particular structure, the transition temperature T_t for this disordering is related to the repulsive interaction energy. T_t will be larger than T_c, and an additional phase boundary should exist between T_t at the saturation coverage for a particular structure and T_c, the critical temperature at the critical coverage θ_c. This boundary is believed to be a second-order phase boundary[1,2,7] that meets the first-order boundary in a tricritical or multicritical poin..

b) Substrate Surface Heterogeneity

As mentioned earlier, the thermodynamic limit requires one large ordered region to form, surrounded by a lattice gas, if fluctuations are neglected. For several reasons this may never occur experimentally[12]. There will likely be a large number of nucleation sites on the surface. Orientationally symmetric domains may form. But most importantly, the substrate surface itself may contain extended defects, such as steps, that provide effectively infinite barriers for diffusion, so that the substrate acts like a collection of independent, much smaller surfaces, with an atom initially adsorbed into such a subsurface, or "pot", constrained to remain there. Evidence exists for such substrate disorder,[14] and also for overlayer island size limitations that approximate the "pot" size[12,15].

Two opposite effects on the phase diagram could result. In the simplest case where the substrate extended defects serve only to contain the adatoms without having a significant effect on the total "cohesive energy" of the island, many small, essentially circular islands will form and the transition temperature at any coverage will be lowered, because inclusion of the positive boundary free energy will reduce the stability of the islands. This is similar to melting point lowering observed in very small bulk particles. In the opposite case, where the defect has considerable effect, i.e., where adsorption to the defect lowers

the total free energy, the phase boundary may, in fact, rise, and island boundaries could be concave, as nucleation begins on the defects and the ordered phase grows inward from there.

A different model for the effect of substrate surface heterogeneity assumes that diffusion over defects can occur, and that all the adatoms collect in a few "lakes" or "valleys"[16]. Contrary to the first model, where the adatoms are uniformly dispersed among all the pots and constrained to stay there, the second model will always fill the most favorable pots completely, leaving part of the surface empty. This seems less likely and is in conflict with the frequently observed broadening of LEED reflections at low coverages[6,9-13] This has been discussed in detail elsewhere[12, 17].

III. Thermal Properties of the Chemisorbed Condensed Phase W(110)p(2x1)-O

Although island-forming chemisorption has been observed numerous times, only recently has the effect of temperature on the condensed phase (i.e., the islands) been investigated for a wide range of coverage[6, 10-13]. In our experiments,[6,12,13] LEED measurements were made on W(110)p(2x1)-O, an overlayer structure consisting of doubly spaced close-packed rows parallel to [1$\bar{1}$1] directions, shown schematically in Fig. 3. Superlattice LEED beams were observed already at very low coverage,[6,12,13] indicating the formation of ordered regions of a particular structure and density (i.e., the p(2x1) structure) before the coverage required such a dense structure. These regions grow as the coverage is increased and eventually touch each other, forming boundaries that could be translational antiphase boundaries or boundaries between domains of different orientation[15]. Saturation

coverage for this structure is θ = 0.5, since alternate rows are empty.
Streaking of spots is not observed even at very low coverages, indicating
the ordered regions are on the average round.

For this system phase transitions at constant coverage have been
investigated for a range of coverages 0.1 <θ<1 by measuring the decay of
superlattice beam intensities, J, as a function of temperature[6, 13]. The
transition temperatures, chosen as the inflection points in the intensity
vs temperature curves, are plotted in Fig. 4. It is seen that there
exists a region of nearly constant transition temperatures (460°K) centered
about θ = 0.25. We believe this region can be described in terms of the
Lee-Yang model, as discussed above.

If the atoms occupy bridge-bonded sites, a possible set of necessary
and sufficient interactions to describe the structure, symmetry, and
shape of the p(2 x 1) islands is - ϵ_a, ϵ_b, and - ϵ_{2b} along the directions
shown in Fig. 3. Furthermore, the fact that the islands are round[6, 12]
suggests that - ϵ_a = - ϵ_{2b}, and the fact that alternate rows are empty
requires $|\epsilon_b|<|\epsilon_a|$. Assuming - ϵ_a = - ϵ_{2b}, the Lee-Yang model is directly
applicable to the portion of the diagram for 0<θ<0.5 if one assumes an
overlayer "lattice" site to correspond to a pair of neighboring sub-
strate sites (the two sites to which the adatom is bridge-bonded), as
discussed in the last section, and the two-phase region should be
symmetric about θ = 0.25.

This definition of an overlayer "lattice" site is equivalent to
saying that the repulsive interaction that keeps alternate substrate
sites in the p(2 x 1) structure empty is large relative to the attractive

interaction that leads to the formation of islands. As the coverage is increased, any disordering must eventually include these sites. As already remarked, this makes the phase diagram no longer strictly symmetric about $\theta = 0.25$. The existence of the repulsive interaction produces a true order-disorder transition at $\theta = 0.5$ at a higher transition temperature that is a measure of the difference between the repulsive and attractive interactions. This is observed experimentally[12]. It thus also leads to an additional phase boundary, and changes what would be a critical point at T_c to a tricritical or multicritical point. However, this should not affect the argument presented here as we approach this point either from above or below θ_c, and we ignore this complication.

We therefore describe the region in the phase diagram symmetric about $\theta = 0.25$ and below 460°K by a model consisting of an attractive interaction - $\varepsilon_a = - \varepsilon_{2b}$, where the overlayer lattice is defined as above. Using the Lee-Yang model and fitting the transition temperature, we find - $\varepsilon_a = - \varepsilon_{2b} = -0.069$ eV, from equations 17 and 11. The corresponding calculated phase boundaries are also plotted in Fig. 4.[18]

Experimentally, one observes that the size of the islands never exceeds about 60 Å,[12] a value that is also roughly consistent with measurements of the step density on the W(110) substrate.[14] The limited island size also results in a rounding of the transitions J vs T; a fit to these curves using sums over finite domains again gives about the same island size.[15] Depending on the model one chooses for the effect of the substrate heterogeneity, the phase boundaries may move up or down. Using the simplest model of independent small

terraces or "pots", a reduction in transition temperatures of about

20-30% is expected because of the effect of island boundary energy,

and the ε calculated here would be too low by this factor.

VI. Discussion

It may seem apparent that a quantitative evaluation of the (average) attractive

interaction energy could have been obtained directly from the application

of the Onsager solution (Eq. 10) at θ_c. This is certainly true, although

it has, to our knowledge, been used only to determine repulsive interactions

in saturation-coverage order-disorder transitions where the repulsive

interaction was assumed to be the only interaction present. A demonstration

of the applicability of the Lee-Yang model, as we have done, is required

to extract the attractive interaction. Furthermore, the Lee-Yang model

allows fitting the complete phase boundary, not just the critical point.

If the additional phase boundary due to the higher-density interactions

distorts the phase boundary around θ_c, the Lee-Yang model will not fit the data

there, but should continue to fit the data at lower coverages. Thus it should be

possible to extract the "true" attractive interaction (given still the limitations

of the model). Unfortunately the data are not yet sufficiently complete at low

coverages to evaluate any deviations from "ideal" behavior near θ_c.

In summary, we emphasize the following two points. Islands observed

in chemisorbed layers may in some cases be thought of as analogous to the

liquid phase in gas-liquid condensation. Support for this comes from

Landau and Lifshitz[19], who argue that a critical point could exist for

a system that undergoes a quantitative change in symmetry as the chemisorbed

layer does. This is the basis for the present discussion.

Second, whereas there are other possible models for explaining the behavior of W(110)p(2x1)-O at low coverages, we believe that the Lee-Yang model is the only one that can be solved analytically. The model is easily extended to other structures, as we have pointed out. The assumption of equal-strength interactions at different distances is not inconsistent with the oscillatory behavior found for the substrate-modulated chemical interaction that represents the major contribution to adatom interactions in chemisorption.[20] Even though the required set of interactions may over-simplify the physical situation, (e.g., it is not sufficient for nonbridge-bonded adatoms in a p(2x1) structure and even with this site, the assumption of $\varepsilon_a = \varepsilon_{2b}$ may be too simplistic) we believe the application of this model should give a first-order estimate of the "cohesive" energy or net attractive adatom interaction for other chemisorption systems that form islands at low coverages.

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Figure Captions

Fig. 1   Schematic diagram of a two-dimensional square lattice system in the grand canonical ensemble. Surrounding the lattice is a "gas reservoir" which can absorb from or provide gas atoms freely to the system. $-\epsilon$ is the attractive interaction energy.

Fig. 2   Phase boundaries of a lattice gas system with an attractive nearest-neighbor interaction. The area under the curve OAB is the coexistence region for vapor phase and islands. Above T_c only the gas phase is stable. Curve OAB is symmetric about the critical coverage $\theta_c = 0.5$.

Fig. 3   Schematic diagram of a p(2x1) overlayer island on a bcc(110) substrate with the overlayer atoms (x) occupying bridge bonding sites with respect to the substrate (•). a, b are substrate unit mesh vectors. The adatom interaction energies ϵ_a and ϵ_{2b} are assumed equal in the calculation. x's in the gas phase indicate lateral vapor pressure of the island.

Fig. 4   Phase diagram for W(110)p(2x1)-O, where $\theta = 0.5$ is the saturation coverage and $\theta_c = 0.25$ is the critical coverage. The experimental points are compared with the model theoretical curve OAB, taking $T_c = 460°K$ and $\epsilon = -0.069$ eV. The required additional phase boundary is shown between the two-phase region and the saturation-coverage order-disorder transition at $T_t = 720°K$. All data points are for the (1/2 1/2) beam at normal incidence. ◆: 52 eV; x: 80 eV; •: 115 eV.
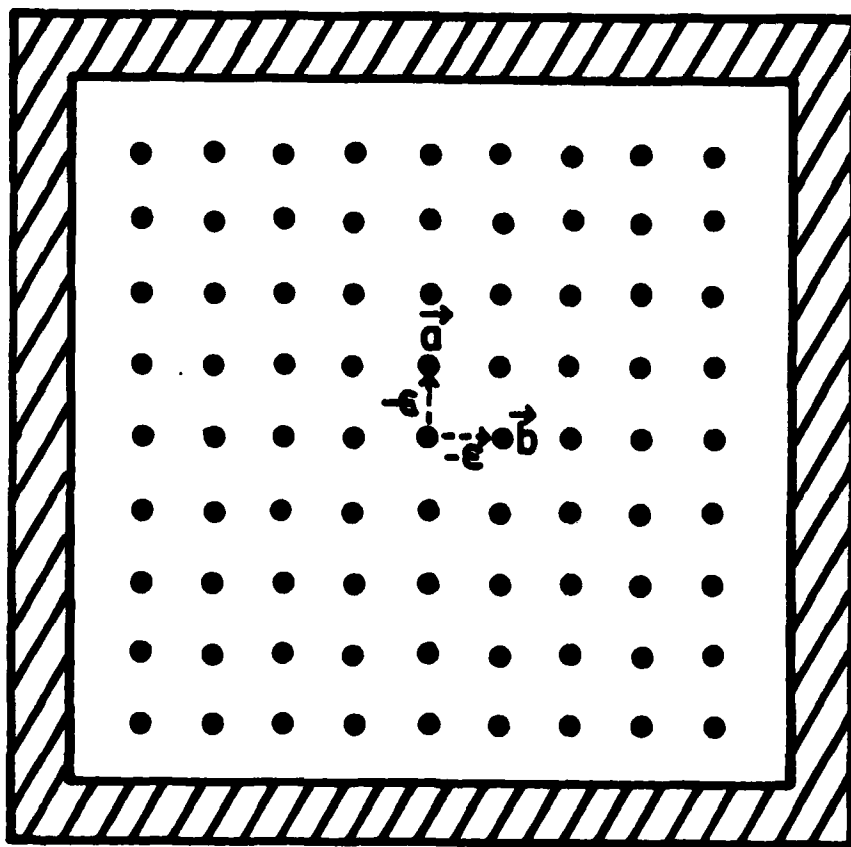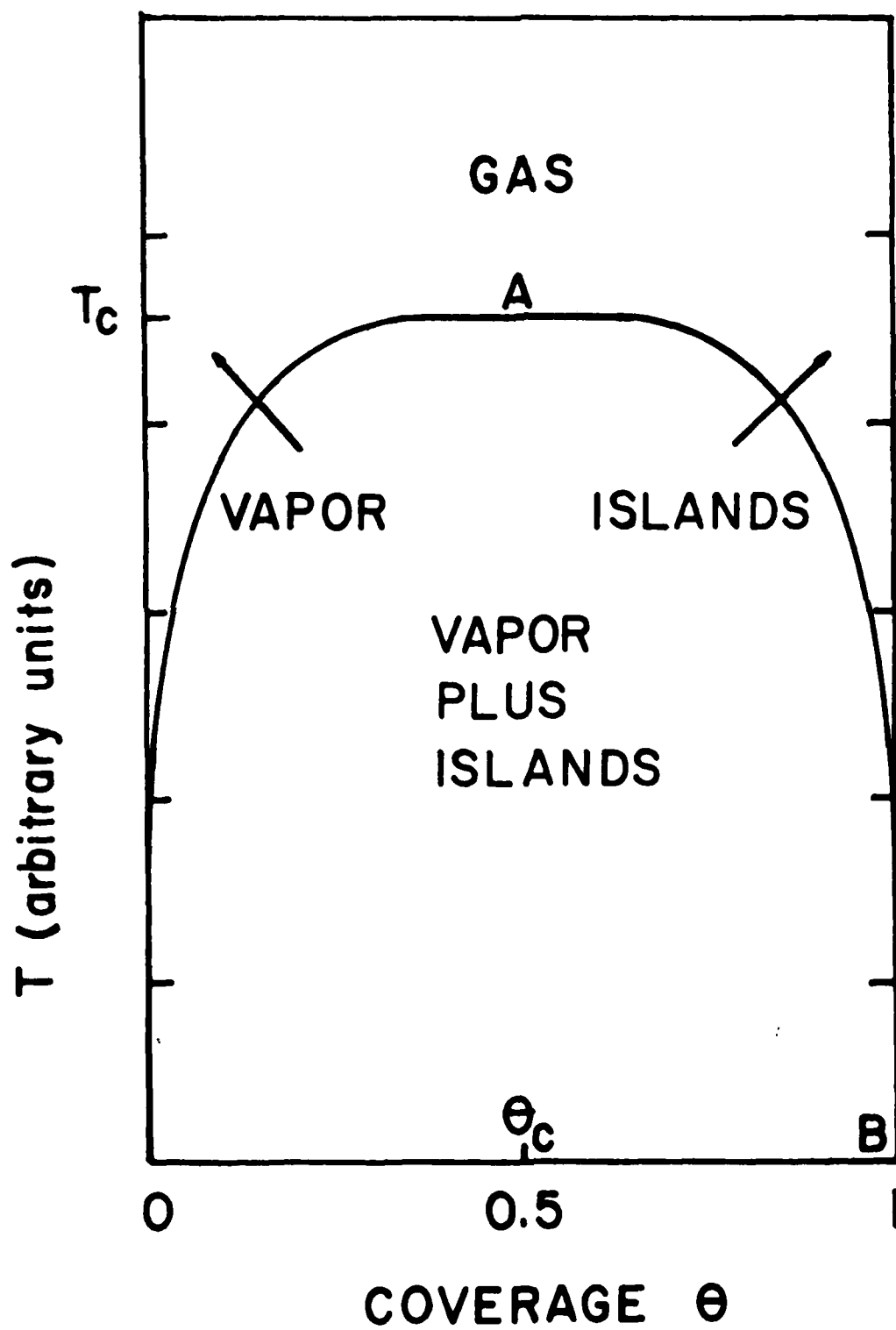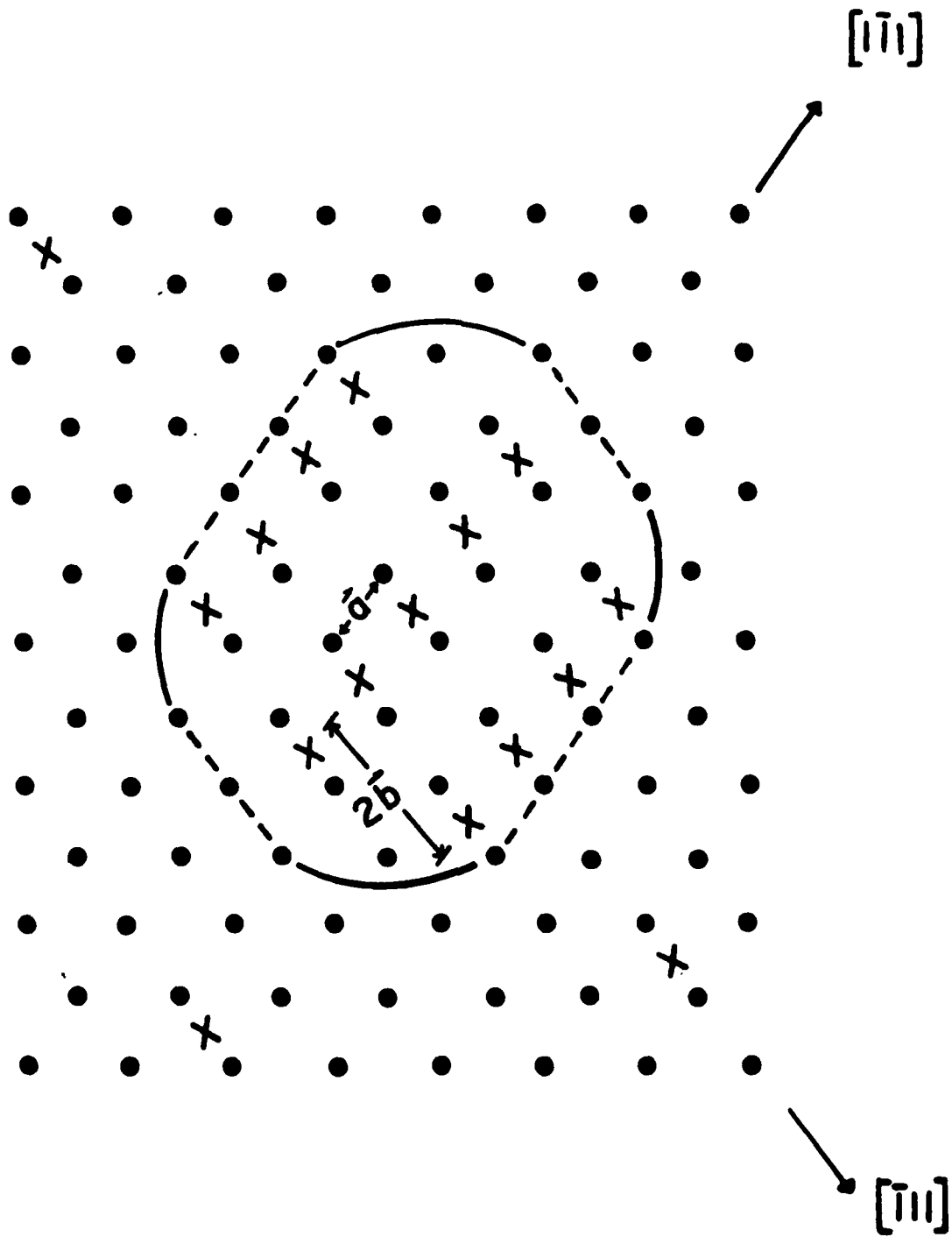
Figure 1

Figure 2

Figure 3

Figure 4